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Influence of the Ligand Backbone in Pincer Complexes: Indenediide-, Indolyl-, and Indenyl-Based SCS Palladium Complexes

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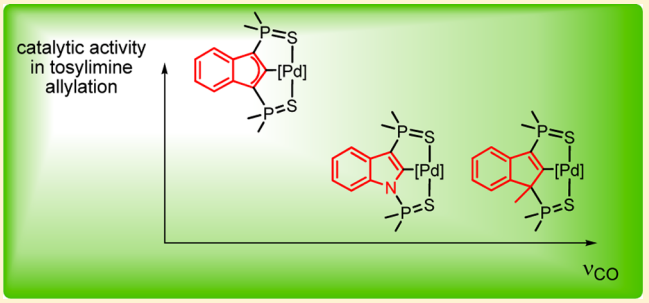
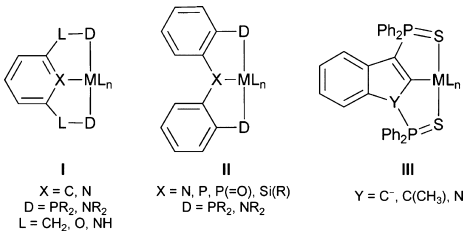
Supporting Information

ABSTRACT: A new pincer ligand featuring an indolyl backbone was prepared and coordinated to palladium. The properties of related indenediide-, indenyl-, and indolyl-based complexes have been compared by spectroscopic and structural means. Modulation of the ligand backbone was shown to significantly influence the electron density at Pd. Its impact on catalytic performance has been illustrated in the Pd-catalyzed imine allylation. The higher the electron density at Pd, the more active the SCS pincer complex.



The stereoelectronic properties of transition metal complexes can be finely tuned by modulating the surrounding ligands, and this plays a fundamental role in organometallic chemistry. The spectacular developments achieved over the past decade with pincer complexes nicely illustrate how the properties and reactivity of a metal can be altered and adjusted through ligand modifications.[1] Here, complexes of types **I** and **II** (Chart 1) are noteworthy examples,

Chart 1. Schematic Representation of Pincer Complexes I–III



and an impressive body of work has been carried out to develop and evaluate new DXD ligand frameworks.[2,3] Not surprisingly, these variations mainly involve the central donor atom and the lateral donating groups (the donor atom, its substituents, and the linker toward the central moiety). Modulations of the pincer ligand without directly affecting the coordination sites are comparatively rare and usually rely on varying the substitution pattern of the remote backbone.[4] Such variations offer the opportunity to fine-tune the electronic properties of the metal while retaining identical structural and steric features.

In this context, we report here a comparative study of SCS palladium pincer complexes of type **III**. They all feature the same framework (two thiophosphinoyle side arms and a central benzannelated five-membered ring) and only differ in the nature of the ligand backbone. As an extension of our work on indenediide and indenyl systems [Y = C$^-$ and C(CH$_3$)],[5] a new pro-ligand deriving from indole (Y = N) has been prepared and coordinated to Pd. The nature of the ligand backbone has been shown by NMR, IR, and X-ray diffraction analyses to substantially influence the properties of complexes **III**, in particular the electron density at Pd. Catalytic tests on imine allylation have also been carried out, and the electron-rich Pd indenediide complex surpassed the indenyl- and indolyl-based systems.

RESULTS AND DISCUSSION

The new pro-ligand **1** was prepared in one pot from indole. The first diphenylphosphino group was introduced by metalation of C3 with MeMgBr followed by reaction with Ph$_2$PCl,[6] while the second one was introduced at N using NEt$_3$ as base and again Ph$_2$PCl. After oxidation with S$_8$ and workup, **1** was isolated in 64% overall yield as a white solid. Coordination to palladium was envisioned by direct C–H activation, as readily achieved upon reaction of the related indene-based pro-ligands with [Pd(RCN)$_2$Cl$_2$] or [Pd(cod)Cl$_2$].[5a,b] However, no reaction took place in the case of **1**, even after prolonged heating. To favor the coordination of the two pending sulfur atoms, the use of cationic Pd precursors was then considered.[4a] Gratifyingly, pretreatment of [Pd(CH$_3$CN)$_2$Cl$_2$] with two equivalents of AgBF$_4$ allowed a smooth reaction to occur with **1**. Complex **2** was thereby obtained in 57% yield as a red-orange powder (Scheme 1).

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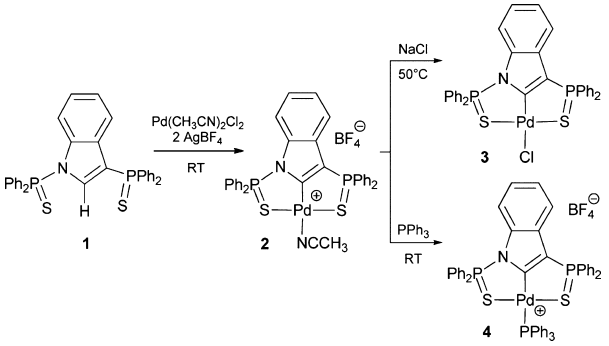
Scheme 1. Coordination to Pd of the Indole-Based Pincer Ligand 1



The coordination of the two thiophosphinoyl side arms is apparent from the downfield shift of the corresponding ^{31}P NMR resonance signals (δ 73.3 and 48.3 ppm for complex **2**, vs 59.5 and 29.9 ppm for the pro-ligand **1**). In addition, metalation of C2 is supported by the disappearance of the associated ^{1}H NMR signal (δ 6.59 ppm for **1**) and the appearance of a C_q signal at 178.3 ppm in the ^{13}C NMR spectrum. The coordination sphere of Pd is completed by an acetonitrile molecule, and the respective NMR signals are clearly identified at δ ^{1}H 2.27 and δ ^{13}C 3.7 ppm. To unequivocally confirm the molecular structure of **2**, crystals were grown by slow evaporation of a dichloromethane solution at room temperature, and an X-ray diffraction study was carried out (Figure 1).

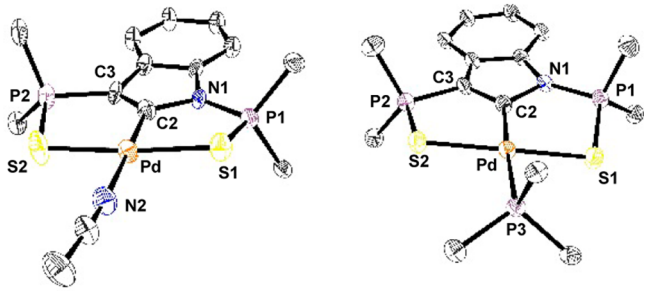


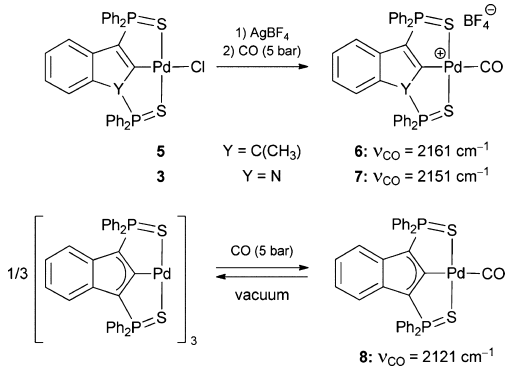
Figure 1. Ellipsoid drawing (30% probability) of the molecular structure of **2** (left) and **4** (right). For clarity, the tetrafluoroborate counteranion, lattice solvent molecules, and hydrogen atoms are omitted, and the phenyl groups at phosphorus are simplified.

The Pd center is in a square-planar environment, with acetonitrile in *trans* position to C2 [PdN 2.077(3) Å, NC 1.129(4) Å, and PdNC 174.2(3)°].[7] The SP(indolyl)PS ligand framework is essentially planar and only slightly tilted with respect to the coordination plane around Pd.

Displacement of acetonitrile at Pd was then studied as a means to vary the coligand in *trans* position to the indolyl moiety. Accordingly, treatment of **2** with sodium chloride in tetrahydrofuran at 50 °C yielded the chloro complex **3**, which could not be obtained directly from **1** and $[Pd(CH_3CN)_2Cl_2]$. Upon exchange of CH_3CN for Cl at Pd, the ^{31}P NMR signals remain essentially unchanged (δ 74.0 and 50.6 ppm), but the ^{13}C NMR signal for C2 shifts to higher field by about 10 ppm (δ 167.4 ppm). Triphenylphosphine also reacts cleanly with **2** in dichloromethane at room temperature to readily afford complex **4**. The ^{31}P NMR spectrum displays an AMX pattern, as expected for two inequivalent thiophosphinoyle side arms (δ 75.2 ppm, d, J_{PP} = 41 Hz and δ 52.9 ppm, d, J_{PP} = 41 Hz) and a coordinated PPh_3 (δ 18.3 ppm, pseudo-t, J_{PP} = 41 Hz). In our series of Pd complexes, a very slight but progressive upfield shift of the ^{31}P NMR resonance is noted (δ 18.9 and 18.7 ppm for the indenyl-based complexes,[5b] δ 18.3 ppm for the indolyl-based complex, δ 17.6 ppm for the indenediide-based one[5b]). The small magnitude of this shift does not allow drawing definite conclusions on the electronic properties of the three ligands.[8] Complex **4** has been analyzed by X-ray diffraction (Figure 1),[9] and its geometric features have been compared with those of the related indenyl and indenediide complexes. The rigid chelating SCS coordination induces quasi invariant Pd−C2 bond distances [2.009(4) Å with indenyl, 2.005(3) Å with indolyl, and 1.997(9) Å with indenediide]. The Pd−PPh_3 bond distance also lies within a narrow range, with a slight increase from the indenyl [2.3593(10) Å] and indolyl [2.3587(8) Å] complexes to the indenediide one [2.380(2) Å].[5b] These data suggest very little, if any, variation of the *trans* influence in the ligand series (indenyl, indolyl, indenediide).[10]

To precisely assess and compare the electronic properties of the three SCS Pd pincer complexes, we then turned to the corresponding carbonyl complexes (Scheme 2). Infrared

Scheme 2. Synthesis and IR Data of the Pd Carbonyl Complexes 6−8



analysis of carbonyl complexes is widely used to probe the electronic properties of ligands, giving an overall estimate of σ-donation and π-back-donation.[11] Such studies most frequently involve Rh and Ni, which readily form carbonyl complexes, but more rarely Pd, whose carbonyl complexes tend to be labile due to weak Pd to CO back-donation.[12] The Pd carbonyl complexes **6** and **7** deriving from the indenyl and indolyl pincer ligands, respectively, were prepared from the corresponding chloro complexes. The chloride at Pd was abstracted with $AgBF_4$, and the reaction vessel was then pressurized with CO. According to ^{31}P NMR monitoring, the reaction requires 5 bar of CO to reach completion. The CO ligand is too labile to enable isolation,[13] but the Pd carbonyl complexes were unambiguously authenticated by NMR spectroscopy (a diagnostic P-coupled ^{13}C NMR signal is found at δ ∼176 ppm). The corresponding indenediide complex **8** cannot be prepared following the same route.[14] Instead of the chloro precursor, the trimeric complex $\{Pd[Ind(Ph_2P{=}S)_2]\}_3$ featuring labile sulfur bridges was used as precursor, and complex **8** was quantitatively formed under 5 bar of CO. Complexes **6**−**8** stand as rare examples of Pd carbonyl pincer complexes.[15] Their FT-IR spectra were recorded under a CO atmosphere, and the corresponding ν_{CO} bands were found at 2161 cm^{-1} for the indenyl complex **6**, 2151 cm^{-1} for the indolyl complex **7**, and 2121 cm^{-1} for the indenediide complex **8**. The variation of

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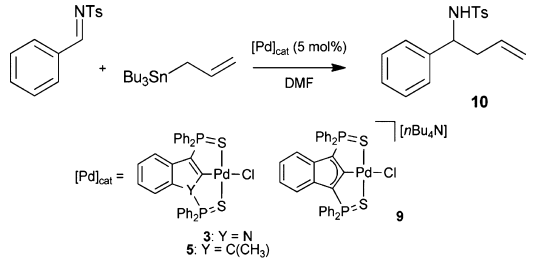
the CO stretching frequency parallels that of the ^{31}P NMR chemical shift and Pd−P distance in the PPh_3 complexes and clearly indicates an increase of the electron density at Pd in the series indenyl ≤ indolyl < indenediide. This is consistent with the electronic properties of the ligand backbone, whose central fragment can be formally described as a vinyl, an enamine, and an allyl anion, respectively. Despite the structural similarity of the three complexes, the variation is relatively large, with a shift of the ν_{CO} band by up to 40 cm^{-1}.[16]

The comparison of the indenyl, indolyl, and indenediide complexes described herein shows that slight variations of the ligand backbone can have a significant influence electronically, while retaining very similar structural and steric features. This is an attractive strategy to finely tune the properties of pincer complexes and a complementary approach to the modulation of the donor moieties, as more commonly employed.

To illustrate how such backbone modulations can influence catalytic properties, preliminary tests were performed in the Pd-catalyzed allylation of imines.[17] Recently, Szabó et al. have shown that PCP pincer ligands are well suited for this Pd-catalyzed transformation, and a catalytic cycle involving an η^1-allyl complex as key intermediate was proposed.[18] Our study consisted in comparing the activities of the indenyl, indolyl, and indenediide chloro Pd complexes in the reaction of phenyl tosylimine with allyltributylstannane (Table 1). Initial tests

Table 1. Catalytic Allylation of Phenyl Tosylimine with the SCS Pincer Pd Complexes 3, 5, and 9[a]



run	cat.	solvent	time (h)	temp (°C)	conversion[b] (%)	yield[c] (%)
1	**9**	THF	21	60	72	63
2	**9**	DMF	21	60	94	88
3	**9**	DMF	21	40	88	83
4	**5**	DMF	21	40	63	51
5	**3**	DMF	21	40	41	33
6	**9**	DMF	5	40	70	61
7	**5**	DMF	5	40	37	26
8	**3**	DMF	5	40	39	27

[a]Reactions performed with 0.45 mmol of PhCH=NTs, 0.54 mmol of $n$$Bu_3$Sn(allyl) at 5% mol catalyst loading. [b]Determined by ^1H NMR. [c]Isolated yields.

were carried out at 60 °C in THF and DMF, the usual solvents of choice, with the indenediide complex **9** (runs 1 and 2). The reaction performed significantly better in DMF (88% vs 63% isolated yield after 21 h at 60 °C). The reaction temperature was then decreased to 40 °C (run 3), and the allyl tosyl amine **10** was obtained in only slightly lower yield (83% after 21 h). Under the same reaction conditions (DMF, 40 °C, 21 h), the indolyl and indenyl chloro complexes **3** and **5** showed substantially lower activities, affording **10** in 33% and 51% yields, respectively (runs 4 and 5). When the reactions were stopped after 5 h (runs 6−8), the allyl tosyl amine was obtained in 61% yield with the indenediide complex **9** vs 26% and 27% with the indenyl and indolyl complexes **3** and **5**. These results show that the ligand backbone of the SCS pincer Pd complexes can indeed impact significantly the catalytic properties. The higher catalytic activity of complex **9** may be attributed to the higher electron density induced at Pd by the indenediide backbone (as substantiated by the CO stretching frequencies), increasing the nucleophilic character of the η^1-allyl intermediate complex and favoring its attack on the tosyl imine.[19,20] Finally, it is interesting to note that complex **9** compares well in activity with the PCP chloro Pd complexes {PdCl[1,3-$(Ph_2PCH_2)_2$-phenyl]} and {PdCl[(1,8-$(Ph_2P)_2$-anthracenyl]},[20] despite the presence of weaker donating side arms (thiophosphinoyle vs phosphine).

In conclusion, SCS indolyl-based Pd pincer complexes have been prepared, and their properties have been compared with those of the previously described indenediide and indenyl complexes. The catalytic activity of the three related complexes has been evaluated in the Pd-catalyzed imine allylation. The most active catalyst is the one featuring the most electron-rich Pd atom, as determined by IR analysis of the respective carbonyl complexes. These results illustrate how the modulation of the remote backbone of pincer ligands can impact the electronic and catalytic properties of the ensuing complexes.

EXPERIMENTAL SECTION

Preparation of {Pd(CH$_3$CN)[Indolyl(Ph$_2$P=S)$_2$]}BF$_4$ (2). A suspension of $AgBF_4$ (360 mg, 1.85 mmol) in dry CH_3CN (7 mL) was added to a solution of $[PdCl_2(CH_3CN)_2]$ (236 mg, 0.91 mmol) in dry CH_3CN (3 mL) at rt in the dark. A white precipitate was immediately formed. After 1 h stirring, the yellow solution obtained was filtrated and transferred on a solution of **1** (500 mg, 0.91 mmol) in dry CH_2Cl_2 (10 mL). The mixture was stirred overnight, and a beige precipitate was rapidly formed in an orange solution. Solvents were evaporated, and the product was extracted with CH_2Cl_2 (4 × 15 mL). Finally, the cationic complex was precipitated and washed with pentane (about 100 mL). A red-orange solid was isolated (380 mg, 57%). Mp = 256−258 °C (dec); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87−7.82 (m, 10H, PPh_2), 7.73−7.64 (m, 6H, PPh_2), 7.64−7.58 (m, 4H, PPh_2), 7.18−7.10 (m, 2H, H_{benzo}), 7.07−7.02 (m, 1H, H_{benzo}), 6.75−70 (m, 1H, $H_{5/8}$), 2.27 (bs, 3H, CH_3CN); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 73.3 (s, P_1), 48.3 (s, P_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.3−178.2 (m, C_2), 141.3 (dd, J(P,C) = 10.4, 2.9 Hz, C_4), 136.2−136.0 (m, C_{para}PhP), 135.1−134.9 (m, C_{para}PhP), 132.9 (d, J(P,C) = 12.9 Hz, C_{meta}PhP), 132.4 (d, J(P,C) = 12.2 Hz, C_{meta}PhP), 131.0 (dd, J(P,C) = 14.1, 5.0 Hz, C_9), 130.3 (d, J(P,C) = 14.1 Hz, C_{ortho}PhP), 130.2 (d, J(P,C) = 14.0 Hz, C_{ortho}PhP), 125.4 (d, J(P,C) = 84.6 Hz, C_{ipso}PhP), 124.7 (C_8), 124.4 (C_6),123.3 (d, J(P,C) = 95.7 Hz, C_{ipso}PhP), 121.5 (C≡N), 118.8 (C_5), 112.2 (C_7), 3.7 (CH_3CN); HRMS calcd for $[M]^+$ = $C_{34}H_{27}N_2P_2S_2{}^{106}Pd^+$ 695.01202; found 695.0126. Anal. Calcd for $C_{34}H_{27}BF_4N_2P_2PdS_2$: C, 52.16; H, 3.48; N, 3.58. Found: C, 52.34; H, 3.72; N, 3.24.

Preparation of {PdCl[Indolyl(Ph$_2$P=S)$_2$]} (3). Dry CH_2Cl_2 (5 mL) was added to a mixture of $[PdCl_2(PhCN)_2]$ (141 mg, 0.55 mmol) and $AgBF_4$ (212.5 mg, 1.10 mmol). After 5 min in the dark, a solution of **1** (300 mg, 0.55 mmol) in dry CH_2Cl_2 (10 mL) was added. The reaction mixture was then stirred overnight at rt. The white precipitate was eliminated by filtration. Then, solvents were evaporated, and THF (20 mL) and NaCl (300 mg, 5.5 mmol) were added. The suspension was heated at 50 °C for 48 h. A brown precipitate appeared. The reaction mixture was concentrated (ca. 10 mL), and pentane (60 mL) was added in order to precipitate the product. The brown solid was filtered, and the complex was extracted with CH_2Cl_2 (4 × 20 mL). After evaporation, a clear brown solid was isolated (210 mg, 55%). Mp = 183 °C (dec); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.91−7.80 (m, 10H, H_{PPh}), 7.72−7.64 (m, 6H, H_{PPh}), 7.62−7.57 (m, 4H, H_{PPh}), 7.17−7.16 (m, 1H, H_5), 7.13−7.09 (m, 1H, H_8), 7.00−6.96 (m, 1H, H_6), 6.74−6.72 (m, 1H, H_7); $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2) δ 74.05 (s, P_1),

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50.60 (s, P_2); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 167.4−167.3 (m, C_2), 142.3−142.2 (m, C_4), 134.9 (d, J(P,C) = 3.2 Hz, C_{para}PPh), 133.3 (d, J(P,C) = 3.1 Hz, C_{para}PPh), 132.5 (d, J(P,C) = 12.5 Hz, C_{meta}PPh), 132.1 (C_9), 132.1 (d, J(P,C) = 11.7 Hz, C_{meta}PPh), 129.8 (d, J(P,C) = 14.0 Hz, C_{ortho}PPh), 129.3 (d, J(P,C) = 13.1 Hz, C_{ortho}PPh), 128.5 (d, J(P,C) = 86.3 Hz, C_{ipso}PPh), 126.0 (d, J(P,C) = 95.7 Hz, C_{ipso}PPh), 124.5 (C_8), 123.7 (C_6), 121.2−119.9 (m, C_3), 118.9 (C_5), 112.6 (C_7); HRMS calcd for $[M - Cl]^+ = C_{32}H_{24}NP_2S_2{}^{106}Pd^+$ 649.9881; found 649.9904. Anal. Calcd for $C_{32}H_{24}ClNP_2PdS_2$: C, 55.66; H, 3.50; N, 2.03. Found: C, 55.84; H, 3.72; N, 1.91.

Preparation of {Pd(PPh$_3$)[Indolyl(Ph$_2$P═S)$_2$]}BF$_4$ (4). Dry CH_2Cl_2 (5 mL) was added to a mixture of $[PdCl_2(PhCN)_2]$ (35.4 mg, 0.13 mmol) and $AgBF_4$ (53 mg, 0.26 mmol). After 5 min stirring at rt in the dark, a solution of **1** (75 mg, 0.13 mmol) in dry CH_2Cl_2 (10 mL) was added. Then, the mixture was stirred overnight at rt. The white precipitate was eliminated by filtration, and dry PPh_3 (36 mg, 0.14 mmol) was added directly to the mixture. Complex **4** tends to decompose upon workup and was thus characterized without purification. Suitable crystals for X-ray diffraction were obtained after concentration, filtration, and slow diffusion of a pentane/CH_2Cl_2 mixture. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.85−7.33 (m, 32H, phenyl), 7.32−7.28 (m, 1H, H_5), 7.26−7.23 (m, 2H, H_{Ph} and H_8), 7.17−7.11 (m, 3H, H_{Ph} and H_6), 6.82 (dd, 1H, J(P,H) = 8.3 Hz, 2.3 Hz, H_7); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2) δ 75.22 (d, J = 41.5 Hz, P_1), 52.85 (d, J = 41.3 Hz, P_2), 18.34 (t, J = 41.5 Hz, P_3); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 177.1 (ddd, J(P,C) = 144.8 Hz, 46.4 Hz, 21.6 Hz, C_2), 142.2−142.1 (m, C_4), 135.5−124.7 (m, C_{Phenyl}), 132.0−131.9 (m, C_9), 124.4 (C_8), 124.1 (C_6), 121.4 (dd, J(P,C) = 125.3 Hz, 11.9 Hz, C_3), 119.1 (C_5), 112.3 (C_7). Anal. Calcd for $C_{50}H_{39}BF_4NP_3PdS_2 \cdot 2CH_2Cl_2$: C, 53.20; H, 3.69; N, 1.19. Found: C, 53.05; H, 3.52; N, 1.24.

Representative Example of Preparation of a Carbonyl Complex, {Pd(CO)[Indolyl(Ph$_2$P═S)$_2$]}BF$_4$ (6). A suspension of $AgBF_4$ (8 mg, 0.04 mmol) in CD_2Cl_2 (0.8 mL) was transferred over **4c** (25 mg, 0.032 mmol) in a Shlenk in order to generate the cationic species. The mixture was stirred 1 h at rt in the dark. A yellow solution was obtained with a white precipitate. The solution was then filtered in a pressure NMR tube, and CO (5 bar) was added. A full conversion was observed by ^{31}P NMR. IR (CD_2Cl_2): ν_{CO} = 2151 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.94−7.83 (m, 8H, PPh_2), 7.81−7.78 (m, 2H, PPh_2), 7.76−7.72 (m, 6H, PPh_2), 7.68−7.65 (m, 4H, PPh_2), 7.29−7.24 (m, 2H, H_{benzo}), 7.18−7.15 (m, 1H, H_{benzo}), 6.84−6.82 (m, 1H, H_{benzo}); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2) δ 76.7 (s, P_1), 52.3 (s, P_2); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 176.4 (t, J(P,C) = 13 Hz, C_{CO}); 166.8 (dd, J(P,C) = 38 Hz, 17 Hz, C_2), 141.5 (dd, J(P,C) = 10 Hz, 4 Hz, $C_{4/9}$), 136.1 (d, J(P,C) = 3 Hz, C_{para}PhP), 134.4 (d, J(P,C) = 3 Hz, C_{para}PhP), 132.7 (d, J(P,C) = 13 Hz, C_{meta}PhP), 132.3 (d, J(P,C) = 12 Hz, C_{meta}PhP), 131.2 (dd, J(P,C) = 14 Hz, 5 Hz, $C_{4/9}$), 130.3 (d, J(P,C) = 14 Hz, C_{ortho}PhP), 129.8 (d, J(P,C) = 14 Hz, C_{ortho}PhP), 125.9 (d, J(P,C) = 88 Hz, C_{ipso}PhP), 125.2 (C_{benzo}), 125.0 (C_{benzo}), 123.9 (d, J(P,C) = 97 Hz, C_{ipso}PhP), 119.3 (C_{benzo}), 112.2 (C_{benzo}).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data, including crystallographic data for **2** (CCDC 931614) and **4** (CCDC 931615). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) *The Chemistry of Pincer Ligands*; Morales−Morales, D.; Jensen, C. M., Eds.; Elsevier: Oxford, 2007. (b) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

(2) For complexes of type **I** featuring an aryl backbone, see for example: (a) Van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (b) Haibach, M. C.; Kundu, S.; Brookhart, M.; Goldman, A. S. *Acc. Chem. Res.* **2012**, *45*, 947. For complexes of type **I** featuring an pyridine backbone, see for example: (c) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588.

(3) For complexes of type **II** with X = N, see for example: (a) Fan, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 326. (b) Vechorkin, O.; Godinat, A.; Scorpelliti, R.; Hu, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 11777. (c) Zhu, Y.; Smith, D. A.; Herbert, D. E.; Gatard, S.; Ozerov, O. V. *Chem. Commun.* **2012**, *48*, 218. For complexes of type **II** with X = SiR, see for example: (d) Takaya, J.; Kirai, N.; Iwasawa, N. *J. Am. Chem. Soc.* **2011**, *133*, 12960. (e) Ruddy, A. J.; Mitton, S. J.; McDonald, R.; Turculet, L. *Chem. Commun.* **2012**, *48*, 1159. For complexes of type **II** with X = P or P(═O), see for example: (f) Mankad, N. P.; Rivard, E.; Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 16032. (g) Derrah, E. J.; Ladeira, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Chem. Commun.* **2011**, *47*, 8611. (h) Gloaguen, Y.; Jacobs, W.; de Bruin, B.; Lutz, M.; van der Vlugt, J. I. *Inorg. Chem.* **2013**, *52*, 1682.

(4) (a) Bergbreiter, D. E.; Osburn, P. L.; Liu, Y.-S. *J. Am. Chem. Soc.* **1999**, *121*, 9531. (b) Slagt, M. Q.; Rodríguez, G.; Grutters, M. M. P.; Gebbink, R. J. M. K.; Klopper, W.; Jenneskens, L. W.; Lutz, M.; Spek, A. L.; van Koten, G. *Chem.—Eur. J.* **2004**, *10*, 1331. (c) Vabre, B.; Spasyuk, D. M.; Zargarian, D. *Organometallics* **2012**, *31*, 8561.

(5) (a) Oulié, P.; Nebra, N.; Saffon, N.; Maron, L.; Martin-Vaca, B.; Bourissou, D. *J. Am. Chem. Soc.* **2009**, *131*, 3493. (b) Nebra, N.; Lisena, J.; Ladeira, S.; Saffon, N.; Maron, L.; Martin-Vaca, B.; Bourissou, D. *Dalton Trans.* **2011**, *40*, 8912. (c) Oulié, P.; Nebra, N.; Ladeira, S.; Martin-Vaca, B.; Bourissou, D. *Organometallics* **2011**, *30*, 6416. (d) Nebra, N.; Saffon, N.; Maron, L.; Martin-Vaca, B.; Bourissou, D. *Inorg. Chem.* **2011**, *50*, 6378. (e) Nebra, N.; Ladeira, S.; Maron, L.; Martin-Vaca, B.; Bourissou, D. *Chem.—Eur. J.* **2012**, *18*, 8474.

(6) For the selective functionalization of C3 using Grignard reagents, see for example: (a) Reinecke, M. G.; Sebastian, J. F.; Johnson, H. W., Jr.; Pyun, C. *J. Org. Chem.* **1972**, *37*, 3066. (b) Ikunaka, M.; Kato, S.; Sugimori, D.; Yamada, Y. *Org. Process Res. Dev.* **2007**, *11*, 73.

(7) These geometric features are similar to those reported for related complexes. See for example: Evans, D. R.; Huang, M.; Segenish, W. M.; Fettinger, J. C.; Williams, T. L. *Organometallics* **2002**, *21*, 893.

(8) ^{31}P NMR has been occasionally used as a probe to compare the electronic properties of ligands in *trans* position; see Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* **1986**, *25*, 616. However, as chemical shifts can be affected by other factors, conclusions are difficult to draw.

(9) See Supporting Information for details.

(10) *Trans* influence can be at the origin of important differences in reactivity, as recently demonstrated for PCP palladium hydride pincer complexes; see: Gerber, R.; Fox, T.; Frech, C. M. *Chem.—Eur. J.* **2010**, *16*, 6771.

(11) Tollman, C. A. *Chem. Rev.* **1977**, *77*, 813.

(12) Kündig, E. P.; McIntosh, D.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7234.

(13) Under vacuum, CO rapidly dissociates and complexes **6**−**8** give back the corresponding Pd precursors. Pressurization with CO regenerates the carbonyl complexes.

(14) Treatment of the chloro indenediide palladate with silver salts does not induce chloride abstraction but rather leads to bimetallic

complexes. This is reminiscent of what we observed with other electrophilic metal fragments.[5d,e]

(15) (a) Yun, J.-G.; Seul, J. M.; Lee, K. D.; Kim, S.; Park, S. *Bull. Korean Chem. Soc.* **1996**, *17*, 311. (b) Bolliger, J. L.; Blacque, O.; Frech, C. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6514. (c) Bolliger, J. L.; Blacque, O.; Frech, C. M. *Chem.—Eur. J.* **2008**, *14*, 7969. (d) Gerber, R.; Blacque, O.; Frech, C. M. *Chem. Cat. Chem.* **2009**, *1*, 393. (e) Zucca, A.; Petretto, G. L.; Cabras, M. L.; Stoccoro, S.; Cinellu, M. A.; Manassero, M.; Minghetti, G. *J. Org. Chem.* **2009**, *694*, 3753.

(16) Frech et al. have compared the electronic properties of POCOP and P(NH)C(NH)P Pd pincer complexes using the same methodology, and the ν_{CO} band was found to shift by 27 cm^{-1}.[14c]

(17) Selander, N.; Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048.

(18) (a) Solin, N.; Kjellgren, J.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3656. (b) Solin, N.; Kjellgren, J.; Szabó, K. J. *J. Am. Chem. Soc.* **2004**, *126*, 7026. (c) Wallner, O. A.; Szabó, K. J. *Chem.—Eur. J.* **2006**, *12*, 6976.

(19) Szabó et al. have noticed that a proper balance is necessary for pincer complexes to catalyze efficiently this transformation, because the formation and reaction of the η^1-allyl complex have opposite electron demands.[17]

(20) At this point, it is difficult to compare the catalytic efficiency of the indolyl and indenyl complexes because of stability issues. The two systems give identical results after 5 h (within margin error), but when the reactions are pursued over 21 h, a substantially higher yield is obtained with the indenyl over the indolyl complex (63% vs 41%). The indolyl complex **3** tends to decompose over time under the catalytic conditions (as apparent from the formation of black insoluble material).